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NITRIDING OF INDUSTRIAL GLASS SURFACE

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The effect of gas-thermal nitriding of window, medical, electrovacuum, and crystal glass surfaces on the service properties of glass is investigated. The hydrophoby, water resistance, microhardness, impact viscosity, and heat resistance of glasses are analyzed depending on the duration of nitriding involving different nitrogen-bearing gas reactants. Technological recommendations for gas-thermal nitriding of glass articles in industrial conditions are issued.

The gas-thermal treatment of glass surface makes it possible to significantly improve its service properties without modifying the glass composition and to obtain better-quality products. The problem of improving vertically drawn sheet glass quality is topical, since its surface becomes corroded under unfavorable storage and service conditions. Container and household glasses contacting aqueous solutions in service also need anticorrosion protection, especially of the inner surface. Electrovacuum glass parts of incandescent bulbs in assembly do not always withstand multiple temperature differences and mechanical impacts, which decreases the yield of acceptable product.

The most important parameters of industrial glasses are chemical resistance and mechanical strength, which can be improved by different methods. The known methods of cation modifying of glass surface (ion exchange, leaching, implantation) do not affect its anion component, i.e., the glass-forming skeleton which to a great extent determines glass properties.

A method of anion modification of glass structure, namely, nitriding oxide glass with the formation of a mixed oxynitride matrix is of great interest. The replacement of double-bond oxygen by three-bond nitrogen in the surface layer structure decreases the number of hydrophilic centers on the glass surface, leads to the consolidation of structure and, accordingly, increases glass density and chemical resistance and improves its thermophysical and mechanical properties [1, 2]. It should be noted that surface nitriding is effective for glasses with a weakly bonded matrix: borate, phosphate, or plumbate [3]. For silicate glasses the most effective method is nitriding glass melt with the formation of stronger silicon-nitride bonds [4].

The optimum method of introducing nitrogen in the surface glass layer is gas-thermal treatment in a medium of nitriding gaseous reactants without the formation of reaction products on the glass surface (which occurs in other treatment methods), i.e., without disturbing its optical clarity. The most technologically suitable reactants are the gaseous compounds of the reaction-capable nitrogen, which can be easily combined with the process of thermal treatment (annealing, hardening) of glass products.

The degree of nitriding of glass structure depends on the quantity of nitrogen introduced, which depends on the glass composition and the state of its surface, the composition and pressure of the gaseous reactants, the temperature and duration of nitriding.

In the present research industrial glasses of different compositions were subjected to surface nitriding at a temperature close to the vitrification temperature: vertical-drawing window glass, incandescent bulb glass parts, brown medical glass bottles, and crystal glass articles (Table 1). The nitriding gaseous reactants were gaseous N_2 and NH_3, as well as gaseous mixtures $NH_3 + H_2O$ and $NH_3 + HCl$.

It is knows [3] that the temperature of the glass surface has a deciding role in nitriding, The optimum temperature interval for nitriding is the annealing interval, which makes it possible to perform a long-term exposure without the deformation of glass.

It was earlier experimentally found that the temperature of nitriding glass surface virtually coincides with the upper annealing temperature [3, 4]. The lower temperature of nitriding electrovacuum glass is due to the small thickness of the glass article walls (less than 1 mm), which causes their deformation at higher temperatures.

The duration of the nitriding process is determined by the diffusion interaction of the gas reactant with the glass surface. After a certain time, a further action of the nitrogen-bearing gaseous reactant on glass becomes noneffective, since the modified surface layer with a consolidated structure limits the penetration of the gaseous reactant into the glass

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TABLE 1

Glass	Nitriding temperature, °C	Mass content, %						
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
Vertical drawing window, of thickness 4 mm	540	72.6	1.6	0.1	7.5	3.6	14.0	–
Electrovacuum S-96*	520	71.8	0.5	0.1	5.5	3.5	15.6	1.0
Medical OS-1	540	73.0	1.3	–	6.0	4.0	15.7	–
Crystal**	500	59.0	–	–	–	–	–	16.0

* Besides glass S-96 contained 2.0% BaO.

** Besides crystal glass contained 24.0% PbO and 1.0 % ZnO.

depth [3, 5]. Based on earlier experiments in nitriding optical silicate glass [4] and taking into account industrial glass-annealing schedules, the gas-thermal nitriding involving more chemically active reactants (ammonia and its mixtures) lasted 0.5 h, and involving the more inert nitrogen lasted 1 h. The gaseous N_2 in nitriding physically dissolves in the surface layer and chemically reacts with oxygen from the glass skeleton [4]. Therefore, to intensify the adsorption of N_2 molecules in the surface glass layer, the gaseous nitrogen is supplied under an excessive pressure of 0.1 – 0.2 MPa.

After gas-thermal nitriding, the service properties of glass articles related to the state of their surface were analyzed: corrosion resistance (hydrophoby and water resistance), microhardness, impact viscosity, and heat resistance.

The surface hydrophoby was estimated based on the contact wettability angle in distilled water measured with a KM-8 cathetometer. The water resistance of glass was determined by boiling samples in distilled water for 1h and subsequent titration with 0.01 N HCl solution with a measurement error of 5%.

The microhardness of glass was measured on a PMT-3 microhardness meter with a 50 g load on the indentor, and the impact viscosity of electrovacuum glass articles (tubes and rods) on a pendulum testing machine. The thermal resistance of articles to a negative thermal shock was measured by throwing heated samples into water.

It can be seen from the data in Table 2 that the contact wettability angle of nitrided glass increases and reaches maximum values after nitriding with the gas mixture of NH_3 + HCl. In the more hydrophilic crystal glass the surface hydrophoby increases to a larger extent (by 75%) than in window glass (by 50%). The increased hydrophoby of glass may be caused by a decreasing quantity of hydrophilic centers in the surface layers. Presumably these hydrophilic centers are primarily hydroxyl groups, non-bridge oxygen ions, and alkali metal cations. Furthermore, OH-groups on the glass surface react with hydrogen protons that arise in the fission of NH_3 and HCl molecules, form H_2O molecules, and leave the surface glass layer [4].

The NH_3 + HCl gaseous mixture imparts hydrophoby to glass surface more perceptibly than other reactants do, since chlorine ions simultaneously react with alkali metal cations and form an easily washable white chloride tarnish, i.e., leaching of the surface glass layers occurs simultaneously with nitriding. It should be noted that the tarnish arises on window glass surface and is absent on crystal glass, which points to the absence of reaction between the chloride component of the mixture and potassium-lead-silicate glass.

The measurements of water resistance indicated that the most sensitive to various nitriding reactants is crystal glass, which has a weakly bound structure (although its water resistance is high due to the double-alkali effect). After nitriding its water resistance is doubled (after treatment in NH_3 + H_2O) or grows 4-fold (NH_3 + HCl). The specified gas mixtures have an integrated effect on the glass surface: leaching (H_2O, HCl) and nitriding (NH_3).

TABLE 2

Nitriding conditions		Contact wettability angle, deg		Water resistance, ml 0.01 N HCl			Microhardness, MPa		Impact viscosity, kJ/m², of glass S-96		Heat resistance, °C, of glass S-96
gas reactant	duration, h	window glass (vertical drawing)	crystal glass	window glass (vertical drawing)	OS-1 glass	crystal glass	window glass (vertical drawing)	crystal glass	tubes	rods	
Without nitriding	–	42 ± 3	36 ± 2	0.12	0.59	0.016	5500 ± 50	5460 ± 50	4.9 ± 0.6	5.6 ± 0.6	125 ± 5
N_2 (excessive pressure)	1.0	60 ± 5	40 ± 1	0.11	0.58	0.015	6330 ± 50	6120 ± 50	5.2 ± 0.9	5.8 ± 0.6	165 ± 5
NH_3	0.5	52 ± 2	37 ± 2	0.10	0.45	0.012	6150 ± 50	5770 ± 50	7.7 ± 1.7	7.7 ± 1.8	130 ± 5
$NH_3 \pm H_2O$	0.5	49 ± 3	52 ± 1	0.10	0.48	0.009	6120 ± 50	6180 ± 50	5.6 ± 0.7	6.7 ± 0.9	140 ± 5
$NH_3 \pm HCl$	0.5	65 ± 4	63 ± 1	0.03	0.18	0.004	6440 ± 50	6650 ± 50	7.3 ± 1.2	7.2 ± 1.0	150 ± 5

The water resistance of window and medical glass significantly grows only after nitriding with the $NH_3 + HCl$ mixture (3 – 4 times). These glasses have a white sodium chloride tarnish after nitriding, which points to leaching. The water resistance of glasses considered grows not only due to leaching, since there is no tarnish on crystal glass and yet its water resistance grows. This is accounted for by the chemical reaction between glass and ammonia, which replaces oxygen without forming reaction products on the surface. Such components of nitriding mixtures as water steam and hydrogen chloride vapor do not react chemically with glass and only facilitate the incorporation of nitrogen into the surface layer of glass due to the depolymerization of the skeleton [3].

The microhardness of glass reflects the micromechanical properties of the surface layer and is a structure-sensitive parameter. The microhardness of window and crystal glass after nitriding in different reactants grows by 5 – 20%, most of all after treating with $NH_3 + HCl$ mixture. It should be noted that treatment with gaseous nitrogen under excessive pressure causes a higher increment in microhardness than nitriding with dry and moist ammonia. Apparently, excessive pressure of the gaseous reactant facilitates a higher consolidation of the structure due to the physical dissolution of molecular nitrogen in the surface glass layer to a depth of 20 – 40 nm [5]. The increased microhardness of crystal glass is presumably due to nitriding, since the replacement of oxygen by nitrogen apparently causes shrinking and compaction of the surface. Hydrogen chloride vapor molecules facilitate nitriding, since in the initial stage of interaction they break the oxygen bonds in the surface layer structure.

The impact viscosity of glass is determined by the work done on the destruction of electrovacuum glass tubes and rods of diameter 6 mm. It is known [6] that thermal treatment of silicate glass for 4 h at temperatures below the upper annealing temperature has virtually no effect on the impact viscosity. The lower impact viscosity of glass tubes compared to that of rods made of the same glass is due to their small wall thickness and, accordingly, lower brittleness. The average values of the impact viscosity of rods and tubes after nitriding with gaseous ammonia and $NH_3 + HCl$ mixture are 1.5 times higher than after other nitriding reactants, which indicates the strengthening of surface due to the incorporation of nitrogen into the silicon-oxygen glass skeleton.

The results of testing the heat resistance of electrovacuum glass parts (Table 2) show that these articles have the maximum heat resistance (165°C) after nitriding their surface with gaseous nitrogen under an excessive pressure, and the efficiency of ammonia nitriding grows when mixed with water steam and hydrogen chloride vapor. The maximum heat resistance increment is seen in glass parts after gaseous nitrogen treatment for 1 h, which may be an evidence of par-

tial healing of microcracks under the effect of physically dissolved molecular nitrogen. Heat resistance is closely related to the microhardness of glass, therefore, the presence of a hardened layer even of a small thickness on the glass surface has a favorable effect on its heat resistance. Although the increase in heat resistance is insignificant (20 – 40°C), it reflects the general trend of the improvement of glass properties with surface nitriding.

Thus, gas-thermal nitriding of industrial glass surface makes it possible to significantly increase the service parameters of glass articles. The results of nitriding of various glasses suggest the following technological recommendations:

– it is advisable to perform gas-thermal nitriding of glass at the maximum permissible temperature that excludes the deformation of glass, in the course of formation or at the upper annealing temperature;

– for increasing the chemical resistance of glass articles the most efficient is nitriding with gaseous ammonia reactants (ammonia and its mixtures with water steam and hydrogen chloride vapor), which contain more reaction-capable nitrogen and actively react with glass surface;

– to increase mechanical strength and heat resistance of articles, it is advisable to use gaseous reactants (nitrogen, ammonia) under an excessive pressure up to 2 MPa;

– the most acceptable stages of the glass-production process for nitriding are: for sheet glass — the lower sectors of the vertical-drawing machine; for container — the glass-forming machine (feeding the reactant in the course of blow-molding) and the annealing furnace; for glass tubes — the tube-drawing machine (feeding the reactants to the nozzle) and annealing of rods and rubes on a roller conveyor.

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